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Dual Capillary Column System for the Qualitative Gas Chromatography: 2. Comparison between Splitless and On-Column Injection Modes

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A dual capillary column system is described for the simultaneous analysis of a given sample and measurement of retention index (RI) and area ratio (AR) values of each peak on two capillary columns of different polarity, DB-5 & DB-1701 from a single injection. Both capillary columns were connected to either a splitless injector or an on-column injector *via* a deactivated fused-silica capillary tubing of 1 m length and a 'Y' splitter. Both injection modes allowed to measure RI and AR values with high reproducibility (<0.01% RSD) and high accuracy (<10% RE), respectively with the exception that the trace and high boiling solutes required the on-column mode for the accurate quantification and AR comparison. When the dual capillary column system in on-column injection mode was applied to the blind samples containing organic acids, each acid was positively indentified by the combined computer RI library search-AR comparison.

Introduction

Recent advances both in capillary column technology and in instrumentation of gas chromatography (GC) which is primarily a separation technique, make GC to be implemented into routine laboratory qualitative analyses of samples such

as essential oils, organic acids, pollutants and drugs[1-11]. Temperature programmed retention index (RI) system is most conveniently used as criteria for the identification of GC peaks. Confidence in the peak identification is greatly enhanced by matching characteristic RI sets to the reference values followed by comparing area ratio (AR) values of correlated peaks on the columns of different polarity[2,8,12-14].

The accurate quantitative comparisons of correlated peaks on each column require the use of an injection technique which can introduce samples into columns without sample alteration and discrimination[15-17]. In an earlier report[14], we demonstrated that the splitless injection mode was as reproducible as the split mode in RI measurements, while the precision and accuracy in AR measurements and comparisons were much lower in the split mode. The use of the splitless mode was thus required for the more accurate quantitative comparison in the dual capillary column system.

The splitless injection method, however, has drawbacks such as degradation of thermally labile solutes and discrimination against high boiling solutes during the hot vaporization[15-17]. The solution for these problems is to use on-column injection where the syringe needle deposists liquid samples directly inside the columns. The major disadvantage of the on-column mode is to require thorough clean-up of samples. To this problem, the splitless mode is an easy solution because nonvolatile solutes are retained by the packed glass liner. The two injection modes compliment to each other depending on the nature and composition of the sample.

The present work was undertaken to compare the precision and accuracy of the splitless and on-column injection modes in the positive peak identification by RI library search confirmed by AR comparison.

Experimental

Materials. All organic acids tested and triethylamine (TEA) were purchased from commercial vendors such as Sigma (St. Louis, MO, USA) and Aldrich (Milwaukee, WI, USA). The silylation agent, N-methyl-N-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) is available from Pierce (Rockford, IL, USA). All the other solvents and chemicals were of analytical grade. The polarity test mixture supplied from Supelco (Bellefonte, PA, USA) was diluted in isooctane by a factor of 30.

Instrumentation. A Hewlett-Packard model 5890A equipped with a split/splitless capillary inlet system, an on-column inlet system, two flame ionization detectors (FIDs), a 3392A integrator, a HP5895A GC ChemStation, and a Think Jet printer (Hewlett-Packard, Avondale, PA, USA) was used for this study. DB-5 and DB-1701 fused silica capillary columns (J&W Scientific, Rancho, Cordova, CA, USA) were of 30 m×0.25 mm I.D. and 0.241 μm film thickness. For dual capillary column system, a deactivated fused silica tubing (1 m×0.25 mm I.D.) as the retention gap was connected to a common injector and then to each capillary column of the equal dimensions *via* a Chromfit 'Y' sample splitter which allowed the admission of equal sample portions into each column. The each column end was connected to each FID and the two FID signals were processed simultaneously in dual channel mode by the ChemStation.

For the analysis of polarity test mixture both in the splitless and on-colum injection modes, oven temperature was held initially at 60℃ for 2 min, then programmed to 160℃ at a rate of 4℃/min. The acid test mixture and blind samples were run at the oven temperature of 60℃ initially, then programmed to 280℃ at a rate of 4℃/min. Purge delay time for the splitless injection mode was 42 sec and the injection volume of splitless and on-column injection modes were 1.0 and 0.2 μl, respectively.

Preparation of Acid Test Mixture and Blind Samples. Prior to GC analyses, samples containing ten different acids after adding methyl linolenate as an internal standard were subjected to silylation to form *tert*-butyldimethylsilyl (TBDMS) derivatives as described in elsewhere[9,14].

RI Library Searching-AR Comparison. *Via* ChemStation BASIC programs, temperature programmed RI values for the sample peaks of each channel were calculated by linear interpolation between the retention times of adjacent hydrocarbon standard (C_8-C_{30} in isooctane) co-injected with samples. And they were compared with those previously compiled RI reference library[14] for matches to aid in identifying the unknown peaks as described previously[9]. For the further confirmation of the assigned peaks, area ratios of the correlated peaks on each column were compared. In this case, acceptable maximum percent relative error (% RE) for agreement was limited to 10%[14].

Results and Discussion

In the splitless and on-column injections unlike the split

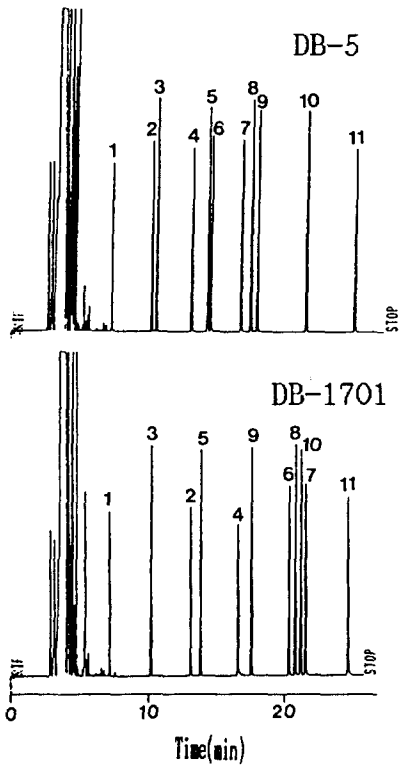

Figure 1. Dual channel chromatograms of a polarity test mixture with a single on-column injection. GC conditions are in the text. Peak identification: 1. nonane; 2. 2-octanone; 3. decane; 4. 1-octanol; 5. undecane; 6. 2,6-DMP; 7. 2,6-DMA; 8. naphthalene; 9. dodecane; 10. tridencane; 11. tetradecane.

Table 1. Retention Index Reproducibility in the Splitless and On-Column Injection Modes on DB-5 and DB-1701

Compound	Splitless mode		On-column mode	
	Mean RI± SD (% RSD)*		Mean RI± SD (% RSD)*	
	DB-5	DB-1701	DB-5	DB-1701
2-Octanone	988.85± 0.04 (0.004)	1080.43± 0.02 (0.002)	988.89± 0.02 (0.002)	1080.43± 0.03 (0.003)
1-Octanol	1068.34± 0.03 (0.002)	1173.36± 0.03 (0.003)	1068.55± 0.02 (0.002)	1173.66± 0.02 (0.002)
2,6-DMP[a]	1106.31± 0.04 (0.004)	1276.40± 0.03 (0.002)	1106.09± 0.02 (0.002)	1276.45± 0.03 (0.002)
2,6-DMA[b]	1168.19± 0.04 (0.003)	1310.40± 0.04 (0.003)	1167.83± 0.02 (0.002)	1310.05± 0.02 (0.002)
Naphthalene	1187.87± 0.06 (0.005)	1290.16± 0.06 (0.005)	1187.20± 0.03 (0.003)	1289.50± 0.03 (0.002)

*Calculated from the results of ten runs within a day. [a]2,6-dimethylphenol. [b]2,6-dimethylaniline.

Table 2. Comparison of the Splitless and On-Column Injection Modes for Measuring Retention Index on DB-5 and DB-1701

Compound	DB-5			DB-1701		Difference (d_i)
	Retention Index			Retention Index		
	Splitless	On-column	Difference (d_i)	Splitless	On-column	
2-Octanone	988.85	988.89	−0.04	1080.43	1080.43	0
1-Octanol	1068.34	1068.55	−0.21	1173.36	1173.66	−0.30
2,6-DMP	1106.31	1106.09	0.22	1276.40	1276.45	−0.05
2,6-DMA	1168.19	1167.83	0.36	1310.40	1310.05	0.35
Naphthalene	1187.87	1187.20	0.67	1290.16	1289.50	0.66
			$\bar{d}=0.20_0$			$\bar{d}=0.13_2$
			$S_d=0.34_4$			$S_d=0.36_9$
			$t^*=1.30$			$t^*=0.80$

*$t=(\bar{d}/S_d)\times\sqrt{n}$. The tabulated t values at 50 and 80% confidence levels for the four degrees of freedom are 0.741 and 1.533, respectively.

Table 3. Area Ratio Reproducibility in the Splitless and On-Column Injection Modes on DB-5 and DB-1701

Compound	Splitless mode		On-column mode	
	Mean AR[a]± SD (% RSD)[b]		Mean AR[a]± SD (% RSD)[b]	
	DB-5	DB-1701	DB-5	DB-1701
Nonane	56.71± 0.83 (1.5)	53.08± 1.06 (2.0)	55.97± 0.30 (0.5)	52.57± 0.17 (0.3)
2-Octanone	70.61± 1.28 (1.8)	67.40± 1.02 (1.5)	72.50± 0.49 (0.7)	69.35± 0.36 (0.5)
Decane	93.27± 1.28 (1.4)	88.16± 1.22 (1.4)	91.35± 0.45 (0.5)	86.79± 0.30 (0.3)
1-Octanol	66.12± 1.34 (2.0)	62.78± 1.88 (3.0)	76.61± 0.85 (1.1)	73.17± 1.85 (2.5)
Undecane	98.26± 0.54 (0.5)	96.16± 0.63 (0.7)	97.20± 0.28 (0.3)	95.54± 0.27 (0.3)
2,6-DMP	77.38± 2.23 (2.9)	78.51± 2.66 (3.4)	82.15± 0.38 (0.5)	83.82± 0.72 (0.9)
2,6-DMA	78.87± 1.72 (2.2)	79.90± 1.76 (2.2)	86.43± 0.88 (1.0)	86.94± 0.66 (0.8)
Naphthalene	99.10± 3.12 (3.1)	100.47± 3.80 (3.8)	105.16± 0.66 (0.6)	105.94± 0.58 (0.5)
Tridecane	101.89± 0.64 (0.6)	101.67± 0.65 (0.6)	103.49± 0.18 (0.2)	102.21± 0.17 (0.2)
Tetradecane	88.87± 1.25 (1.4)	88.89± 1.22 (1.4)	91.98± 0.39 (0.4)	90.23± 0.45 (0.5)

I.S.=*n*-dodecane. [a](peak area of each compound/peak area of I.S.)×100. [b]Calculated from the results of ten runs within a day.

mode, the retention gap[17] accelerates the migration of the condensed flooded sample zone. The zone is then splitted equally and reproducibly from the 'Y' splitter into DB-5 and DB-1701 columns of the equal dimensions where each splitted zone is refocused as a short band prior to chromatographic process.

The precision of RI and AR values measured in the splitless and on-column injection modes was tested using polarity test mixture. Figure 1 shows typical dual channel chromatograms obtained from the simultaneous analysis of the mixture on both columns after a single on-column injection.

RI values of the five chemically active components were

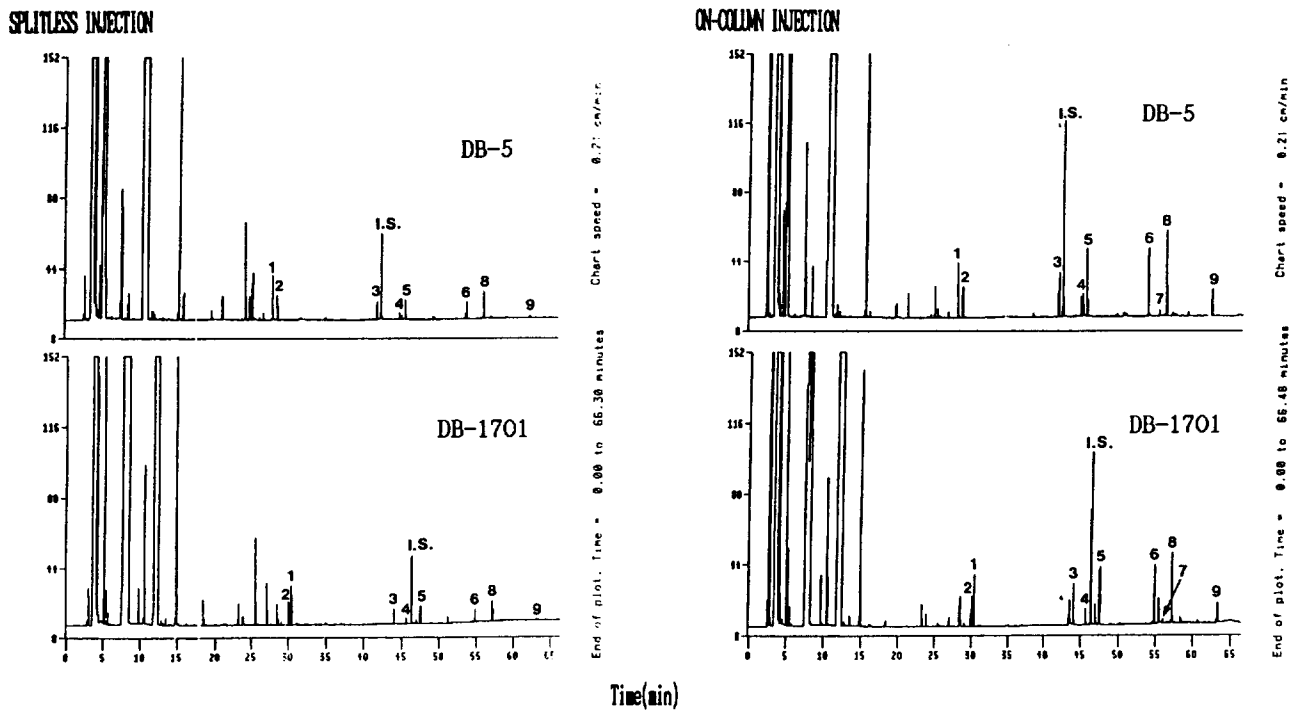

Figure 2. Dual channel chromatograms of an acid test mixture with a single splitless injection and on-column injection. Peak numbers correspond to those in Table 5. GC conditions are in the text.

measured reproducibly with than 0.01% relative standard deviations in both injection modes as listed in Table 1.

Does the on-column injection mode yield a Ri value significantly different from the value measured in the splitless mode? To answer this question, we performed the t test using Student's t on the individual differences between the RI values measured in both methods for each component. The calculated t values on DB-5 ($t=1.30$) and on DB-1701 ($t=0.80$) as seen in Table 2 lie between the tabulated t values at 50% ($t=0.741$) and 80% ($t=1.533$) confidence levels for four degrees of freedom. It would thus be reasonable to conclude that the RI values measured by the two injection modes are not significantly different from each other. Therefore, the RI reference library[14] obtained in the splitless mode could be directly employed for the library search when the on-column mode is used.

AR values of the ten components were measured with good precisions in both injection modes as listed in Table 3. The comparison ratios, Q defined as mean $AR_{DB\text{-}5}/AR_{DB\text{-}1701}$ were calculated to check the accuracy in AR comparison and in theory the true value of Q is unity. The AR values of each component measured on the two columns in both injection modes were well correlated each other with lower than 7% ralative errors as seen in Table 4.

The same tests wre performed using an acid test mixture containing nine organic acids with a wide range of boiling points and concentration. Figure 2 compares two sets of the dual channel chromatograms. The overal FID responses in the on-column mode were significantly higher than those in the splitless mode. Moreover, the trace nonadecanoic acid (peak 7) was not detected and the late eluting erucic and (peak 9) was rarely detected in splitless mode.

There were no significant differences between the two injection modes in the precision of RI measurements and in the individual RI values as well. The splitless mode, however, yielded much higher % RE for the trace and high boiling solutes in the AR comparison as seen in Table 5, indicating the occurrence of discrimination against them during vaporization.

Table 4. Comparison of the Splitless and On-Column Inje Modes for Correlating the Peak Area Ratios Measured on 5 and DB-1701

Compound	Splitless mode		On-column mode	
	Q[a]	% RE[b]	Q[a]	% RE[b]
Nonane	1.068	6.8	1.065	6.5
2-Octanone	1.048	4.8	1.045	4.5
Decane	1.058	5.8	1.053	5.3
1-Octanol	1.053	5.3	1.047	4.7
Undecane	1.022	2.2	1.017	1.7
2,6-DMP	0.986	1.4	0.980	2.0
2,6-DMA	0.987	1.3	0.994	0.6
Naphtalene	0.986	1.4	0.993	0.7
Tridecane	1.002	0.2	1.013	1.3
Tetradecane	0.999_8	<0.1	1.019	1.9

[a] Comparison ratio = mean $AR_{DB\text{-}5}$/mean $AR_{DB\text{-}1701}$. [b] percent relative error = $|1-Q|\times 100$.

The present dual capillary column system in on-column mode was tested with several acid blind samples for the qualitative peak indentification. After RI calculation, library search procedure was performed using the RI reference library obtained in the splitless mode, followed by peak confir-

Table 5. Comparison of Splitless and On-Column Injection Modes with an Acid Test Mixture

No.	Acids	Splitless mode			On-column mode		
		Mean AR[a]		% RE[b]	Mean AR[a]		% RE[b]
		DB-5	DB-1701		DB-5	DB-1701	
1	Benzoic	44.44	50.47	6.0	24.11	25.92	7.0
2	Glycolic	28.05	29.60	5.2	14.37	15.28	6.0
3	Adipic	20.31	19.31	5.2	21.93	22.36	1.9
4	Myristic	7.68	7.36	4.3	9.24	8.84	4.5
5	*p*-OH Benzoic	23.98	23.71	1.1	31.33	31.55	0.7
6	β-Resorcylic	18.56	17.79	4.3	32.48	31.89	1.8
7	Nonadecanoic	nd[c]	nd[c]	·	0.74	0.82	9.8
8	*p*-OH Phenyllactic	32.09	29.63	8.3	42.46	41.55	2.2
9	Erucic	3.67	2.71	35.4	18.30	16.62	10.1

I.S.=methyl linolenate. [a](peak area of each compound/peak area of I.S.)×100. [b]percent relative error=|1−mean AR_{DB-5}/mean AR_{DB-17}|×100. [c]nd=Not detected.

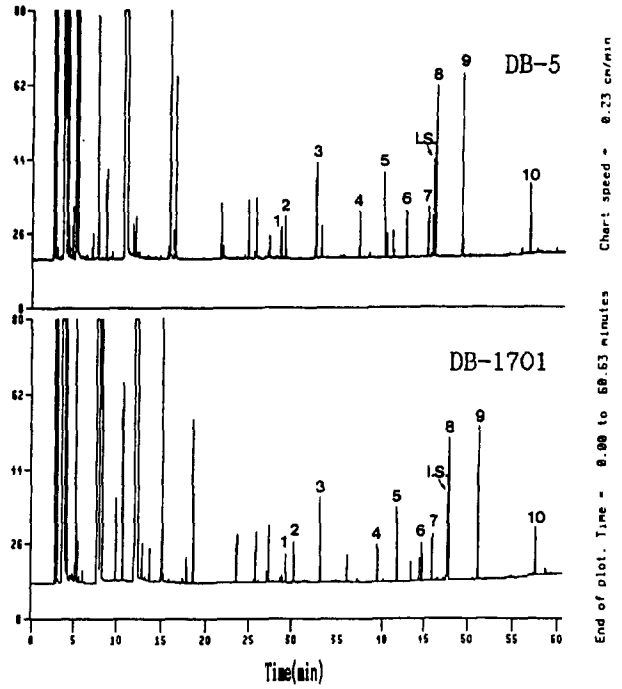

Figure 3. Dual channel chromatograms of acid blind sample I in on-column injection mode. Peak numbers correspond to those in Table 6. GC conditions are in the text.

mation based on the % RE within 10% as described elsewhere[14].

Two of the acid blind samples are exemplified in Figures 3 and 4. Each peak identified by RI match was correctly confirmed by AR correlation except for the tridecanoic acid in sample II as presented in their confirmation reports (Tables 6 and 7). The reason for its high % RE was found due to the coelution of an impurity peak with the acid on DB-1701 column.

In conclusion, we can state that the present dual capillary column system in both injection modes if properly performed

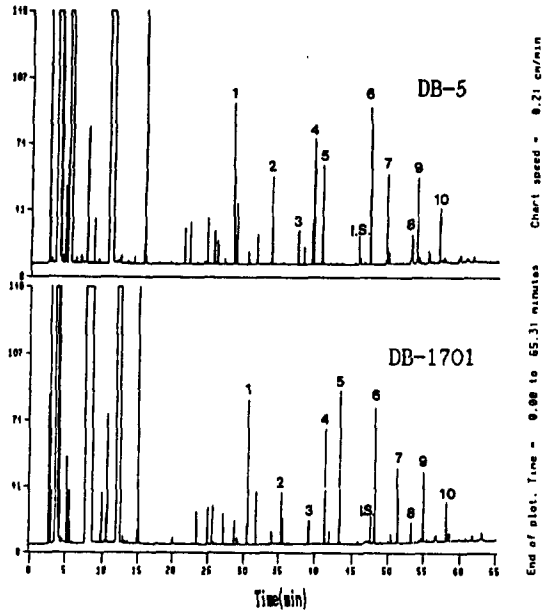

Figure 4. Dual channel chromatograms of acid blind sample II in on-column injection mode. Peak numbers correspond to those in Table 7. GC conditions are in the text.

Table 6. Confirmation Report on Acid Blind Sample I in On-Column Injection Mode

No.	Acids	RI		AMT ? *
		DB-5	DB-1701	
1	Lactic	1489.05	1530.47	Y
2	Glycolic	1505.90	1560.53	Y
3	α-OH Valeric	1619.23	1655.44	Y
4	Itaconic	1788.79	1879.48	Y
5	Mandelic	1902.00	1969.25	Y
6	3-Methyladipic	1988.43	2087.18	Y
7	Myristic	2085.59	2136.96	Y
8	*p*-OH Benzoic	2119.15	2215.11	Y
9	4-OH 3-Methoxy phenylacetic	2246.47	2364.63	Y
10	*p*-OH Phenylacetic	2600.00	2674.14	Y

*Yes for AMT ? when % RE≤10.

Table 7. Confirmation Report on Acid Blind Sample II in On-Column Injection Mode

No.	Acids	RI		AMT ?
		DB-5	DB-1701	
1	Benzoic	1484.61	1572.58	Y
2	Methyl malonic	1656.57	1733.64	Y
3	Fumaric	1786.39	1872.00	Y
4	Glutaric	1855.12	1953.12	Y
5	Tridecanoic	1983.17	2035.59	N*
6	Phthalic	2139.99	2272.98	Y
7	Azelaic	2272.47	2380.42	Y
8	Tataric	2373.33	2457.83	Y
9	Linolenic	2470.10	2555.92	Y
10	Arachidonic	2618.78	2710.33	Y

*No for AMT ? when % RE>10.

permits the combined RI library search-AR comparison to be implemented in routine organic analysis for the positive peak identification without resorting to GC-MS.

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Structural Transition of A-Type Zeolite: Molecular Dynamics Study

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Molecular dynamics (MD) calculations were carried out in order to investigate the effect of MD cell size to predict the melting phenomena of A-type zeolite. We studied two model systems: a pseudocell of $(T_2O_4Na)_n$ ($L=12.264$ Å, $N=84$) and a true-cell of $(SiAlO_4Na)_n$ ($L=24.528$ Å, $N=672$), where T is Si or Al. The radial and bond angle distribution functions of T(Si, Al)-O-T(Si, Al) and diffusion coefficients of T and O were reported at various temperatures. For the true-cell model, the melting temperature is below 1500 K and probably around 1000 K, which is about 600-700 K lower than the pseudocell model. Although it took more time (about 30 times longer) to obtain the molecular trajectories of the true-cell model than those of the pseudocell model, the true-cell model gave more realistic structural transition for the A-type zeolite, which agrees with experiment.

Introduction

In molecular dynamics (MD) simulations, the Newtonian equations of motion are solved numerically for a set of N particles in volume V.[1] Usually, as in Monte Carlo simulations,[2,3] periodic boundary conditions are used to approximate an infinite system. The advantage of the MD approach is that one can study time dependednt single particle properties such as self-diffusion coefficients and the correlation functions. Recently, the extension of MD methods to treate ensembles other than the traditional microcanonical ensemble has attracted considerable attention.[4-6] And the use of Lagrangian which allows the variation of the MD cell shape has demonstrated its usefulness in applications to structural changes in solid state.[7-9]

The melting phenomena of A-type zeolite with temperature changes were studied.[10,11] But the temperature of the structural transition (2100 K) was higher than the experimental result (1100 K). In this study, the effect of the MD cell size on the prediction of the melting phenomena of A-type zeolite is investigated. Using the (N, V, E) ensemble the radial distribution functions and the related properties were calculated for a true-cell model of $(SiAlO_4Na)_n$ ($L=24.528$ Å, $N=672$) at 298, 900, 1500 and 2100 K. And a comparative discussion